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Synergistic extraction and separation of Am(III) and Ln(III) with HBMPPT-sulfoxide-HNO$_3$-toluene system

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Abstract Some sulfoxides (petroleum sulfoxide -PSO, di-n-octyl sulfoxide -DOSO, etc.) were chosen as synergists to study the synergistic effect on the extraction reaction with HBMPPT (4-benzoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-thione) for Am(III), and the synergistic separation for Am(III) and Ln(III). The synergistic extraction ability of PSO is greater than that of DOSO for Am(III). The synergistic complexes may be presented as Am·NO$_3$·(BMPPT)$_2$·HBMPPT·S$_2$ (S indicates PSO or DOSO).

Keywords Synergistic extraction, Am, Ln, HBMPPT
CLC numbers O615.11, O652.62, TL283

1 INTRODUCTION

Americium is a typical transuranium element. The chemical properties of Am(III) are similar to that of trivalent lanthanides, Ln(III). The separation of Am(III) from Ln(III) represents one of the most difficult and important problems in the separation science[1~7]. Actinides (III) overlap in size with Ln(III) and thus two groups have similar charge-to-radius ratios. Choppin[6] considered that Am(III) and Ln(III) both exhibit "hard acid" character and their interaction in solution are mainly ionic in nature. The major difference between these two groups of metals is the tendency of the trivalent actinides to form slightly stronger complexes with ligands coordinating through donor atoms less electronegative than fluorine or oxygen, for example, sulfur or nitrogen[6].

The present work reports the synergistic extraction of Am(III) with HBMPPT (containing soft donor -sulfur)-sulfoxide (PSO or DOSO)-HNO$_3$-toluene system and the separation ability between Am(III) and several trivalent lanthanides.

2 EXPERIMENTAL

2.1 Reagent

HBMPPT was synthesized from HBMPP (4-benzoyl-2,4-dihydro-5-methyl-2- phenyl-3H-pyrazol-3-one) with two procedures[1]. PSO was supplied by Jianghan petroleum Co., containing 9.3% of sulfur amount; DOSO, AR, Tianjian Chemical Reagent Co.;

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^{241}Am(III) is supplied by China Institute of Atomic Energy, the radioactivity being about 3.7 kBq; The other reagents PPO (Baitai Co., Beijing), POPOP (Farco Co., Hongkong), $NaNO_3$ (Beijing chemical reagent Co.,) etc. were all of AR grade.

All aqueous solutions, which contained 0.1 mol/L $NaNO_3$ and certain amount of HNO_3 were made with distilled water. The pH of the aqueous solutions was adjusted with 0.1 mol/L NaOH. The aqueous solutions were pre-equilibrated with toluene.

The organic phase was HBMPPT and PSO (or DOSO) in toluene. In the studies of the dependence of D (distribution ratio) on HBMPPT concentration, the concentration of the PSO (or DOSO) was kept at 0.01 mol/L while the HBMPPT concentration was varied from 0.05 mol/L to 0.40 mol/L.

2.2 Distribution ratio determination

The extraction procedures were as follows: 1 mL of the aqueous phase containing a certain amount of Am(III) and HNO_3 were shaken for 15 min with 1 mL of the organic phase containing a given concentration of HBMPPT and S(PSO, DOSO). After separating by centrifugal governor, the two phases were analyzed by means of ^{241}Am(III) energy spectrum analysis with TRI-carb 2200 CA Liquid Scintillation Analyzer. The distribu*tion ratio of Am(III) was calculated*[2]. *The pH value of aqueous solution was measured* after equilibrium. The experimental temperature was controlled at 25±2°C.

3 RESULTS AND DISCUSSION

3.1 Salting-out effect

Salting-out effect is a result of the reduction in water activity due to the presence of the salt. It is clear that the reduced concentration of available water molecules must have the effect of reducing the net of water exchange of Am(III), improving the energetic requirement for phase transfer reactions[7]. The dependence of distribution ratio of Am(III) on salt concentration at constant HBMPPT and synergist concentration in toluene is shown in Fig.1. Salting-out agent $NaNO_3$ improves the extraction ability of Am(III) strongly. In order to keep the ionic strength in aqueous solution, we chose 0.10 mol/L $NaNO_3$ as the salting-out agent concentration in the next experiment.

3.2 Effect of pH on the distribution ratio

There was no detectable extraction for Am(III) when HBMPPT or synergist was used alone as the pH value studied ($D_1=D_2=0$). When the synergist PSO or DOSO was added to the system, measurable extraction was observed ($D = D_1 + D_2 + D_{12} = D_{12}$). The dependence of distribution ratio of Am(III) on pH at constant HBMPPT and synergist concentration in toluene is shown in Fig.2. The distribution ratio of Am(III) increases with the increase of pH. The relationship of lg$D$-pH is linear with the slope of 2.1 and 1.9 and the relationship coefficient is 0.993 and 0.995 for the PSO and DOSO,

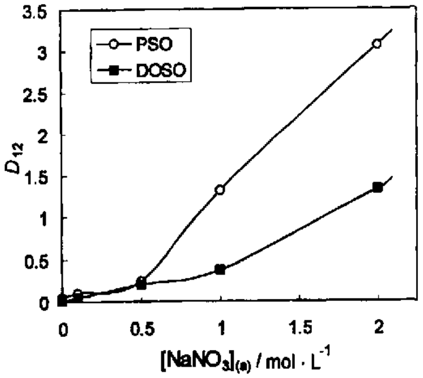

Fig.1 Plots of D versus salting-out agent concentration (pH=3.8, $[HBMPPT]_{(o)}=0.10$ mol/L, $[PSO]_{(o)}=0.03$ mol/L, $[DOSO]_{(o)}=0.01$ mol/L)

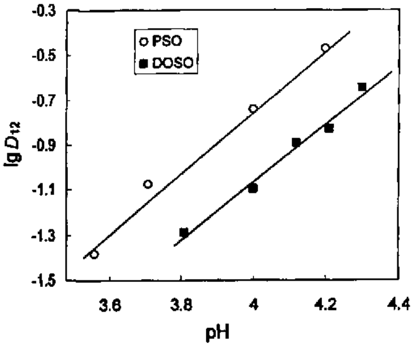

Fig.2 Plots of lg$D$ versus pH ($[HBMPPT]_{(o)}=0.10$ mol/L, $[PSO]_{(o)}=0.03$ mol/L, $[DOSO]_{(o)}=0.01$ mol/L, $[NaNO_3]_{(a)}=0.1$ mol/L)

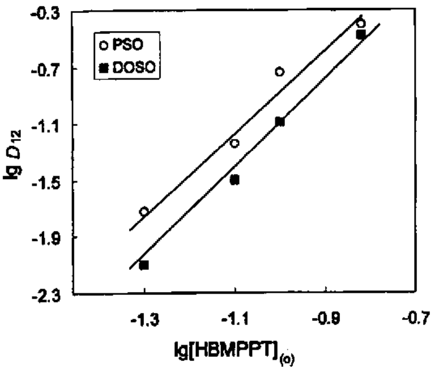

Fig.3 Plots of lg$D$ versus lg$[HBMPPT]_{(o)}$ (pH=3.6, $[PSO]_{(o)}=0.03$ mol/L, $[DOSO]_{(o)}=0.01$ mol/L, $[NaNO_3]_{(a)}=0.1$ mol/L)

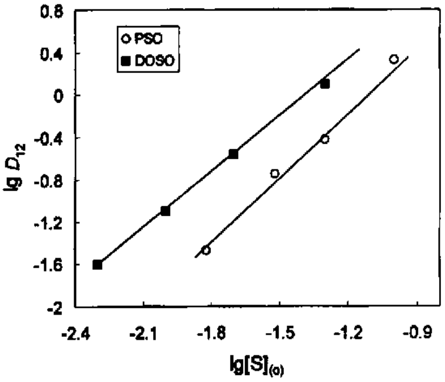

Fig.4 Plots of lg$D$ versus lg$[\text{synergist}]_{(o)}$ (pH=3.6, $[HBMPPT]_{(o)}=0.10$ mol/L, $[NaNO_3]_{(a)}=0.1$ mol/L)

respectively. Because of the strong pH dependency of these extraction and the difficulty of maintaining pH in an unbuffered system, all pH values given were obtained by measurments after equilibrium.

3.3 Effect of HBMPPT concentration on the distribution ratio

An assumption used in the slope analysis method is constancy of the activity coefficient, so that concentration can be used to describe the equilibrium involved in the extraction. The plots of lg$D$ versus lg$[\mathrm{HBMPPT}]_{(o)}$ at a constant pH and $[\mathrm{synergist}]_{(o)}$ (PSO and DOSO) are shown in Fig.3. The distribution ratio increases with the increase of HBMPPT concentration, the relationship of lg$D$-lg$[\mathrm{HBMPPT}]_{(o)}$ is linear with the slope of 2.9 and 3.0, and the relationship coefficient is 0.992 and 0.996 for PSO and DOSO, respectively. This result indicates that the extracted complexes may contain 3 HBMPPT molecules.

3.4 Effect of synergist concentration on the distribution ratio

The plots of lg$D$ versus lg$[\mathrm{synergist}]_{(o)}$ at constant $[\mathrm{HBMPPT}]_{(o)}$ and pH are shown in Fig.4. The distribution ratio increases with the increase of the synergist concentration and the relationship of lg$D$-lg$[\mathrm{synergist}]_{(o)}$ is linear with the slopes of 2.1 and 2.2 for the PSO and DOSO, respectively. The relationship coefficient is 0.998 and 0.994 for PSO and DOSO, respectively. This result suggests that the extracted complexes may contain 2 PSO (or DOSO) molecules.

3.5 Extraction complexes and equilibrium constants

According to the above results obtained for the extraction of Am(III), the extraction process may involve the following synergistic extraction complexes: $\mathrm{AmNO_3}\bullet(\mathrm{BMPPT})_2\bullet$ $\mathrm{HBMPPT}\bullet(\mathrm{PSO})_2$ and $\mathrm{AmNO_3}$ $(\mathrm{BMPPT})_2\bullet$ $\mathrm{HBMPPT}\bullet(\mathrm{DOSO})_2$ for PSO and DOSO, respectively. The synergistic extraction process can be described by the following equation:

$$\mathrm{Am}^{+3}_{(a)}+3\mathrm{HBMPPT}_{(o)}+2\mathrm{S}_{(o)}+\mathrm{NO_3(a)}^- \rightarrow \mathrm{AmNO_3}\bullet(\mathrm{BMPPT})_2\bullet\mathrm{HBMPPT}\bullet\mathrm{S}_{2(o)}+2\mathrm{H}^+_{(a)}$$

where S indicates the PSO or DOSO. The equilibrium constants of this reaction can be described:

$$K = ([\mathrm{AmNO_3} \bullet (\mathrm{BMPPT})_2 \bullet \mathrm{HBMPPT} \bullet \mathrm{S_2}]_{(o)}[\mathrm{H}^+]^2_{(a)})$$

$$/([\mathrm{Am}^{+3}_{(a)}] \bullet [\mathrm{HBMPPT}_{(o)}]^3 \bullet [\mathrm{S}_{(o)}]^2 \bullet [\mathrm{NO}^-_{3(a)}])$$

$$= D \bullet ([\mathrm{H}^+_{(a)}]^2)/([\mathrm{HBMPPT}_{(o)}]^3 \bullet [\mathrm{S}_{(o)}]^2 \bullet [\mathrm{NO}^-_{3(a)}])$$

From the experimental values obtained, The equilibrium constants K are

$$K_{\mathrm{PSO}} = 4.87 \times 10^{-3}; \quad K_{\mathrm{DOSO}} = 2.08 \times 10^{-3}.$$

3.6 Separation of Am(III) and Ln(III)

Typical distribution ratios of Am(III) and Ln(III) are shown in Table 1. The separation coefficient of Am(III) to some trivalent lanthanides are more than 81 and 28 for the PSO and DOSO, respectively.

Table 1 Separation coefficient for Am(III) and Ln(III)

	D_{Am}	D_{Ln}	$\alpha_{Am/Ln}$
PSO	0.81	< 0.01	> 81
DOSO	0.28	< 0.01	> 28

pH=3.6 $[HBMPPT]_{(o)}=0.10$ mol/L, $[PSO]_{(o)}=0.03$ mol/L, $[DOSO]_{(o)}=0.01$ mol/L, $[NaNO_3]_{(a)}=0.1$ mol/L

4 SUMMARY

To the best of my knowledge, the present work reports the synergistic extraction of Am(III) with HBMPPT (containing soft donor-sulfur)-sulfoxide(PSO or DOSO)-HNO_3-toluene system for the first time. Based on the slope analysis, the extracted synergistic complexes may be presented as $AmNO_3$•$(BMPPT)_2$•HBMPPT•$(S)_2$ (S is the PSO or DOSO) for Am(III) ($[HBMPPT]_{(o)}=0.05$–0.2 mol/L) and this system can separate Am(III) from Ln(III) under certain conditions.

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